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First-principles study of polarization and piezoelectricity behavior in tetragonal $PbTiO_3$-based superlattices*

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Using first-principles calculation, the contribution of A-site and B-site atoms to polarization and piezoelectricity d_{33} in the tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices is investigated in this paper. It is shown that $PbTiO_3/KNbO_3$ superlattice has larger polarization and d_{33} than $PbTiO_3/LaAlO_3$ superlattice, because there is stronger charge transfer between A(B)-site atoms and oxygen atom in $PbTiO_3/KNbO_3$ superlattice. In $PbTiO_3/KNbO_3$ superlattice, B-site atoms (Ti, Nb) make larger contribution to the total polarization and d_{33} than the A-site atoms (Pb, K) because of the strong covalent interactions between the transition metal (Ti, Nb) and the oxygen atoms, while piezoelectricity in $PbTiO_3/LaAlO_3$ superlattice mainly ascribes to piezoelectric contribution of Pb atom and Ti atom in $PbTiO_3$ component. Furthermore, by calculating the proportion of the piezoelectric contribution from $PbTiO_3$ component in superlattices, we find there is different response of strain to piezoelectric contribution from $PbTiO_3$ component in two superlattices but still with a value larger than 50%. In $PbTiO_3/KNbO_3$ superlattice, the *c*-axis strain reduces the proportion, especially under tensile condition. Meanwhile in $PbTiO_3/LaAlO_3$ superlattice, $PbTiO_3$ plays a leading role to the total d_{33}, especially under compressive condition, and the proportion decreases as the tensile strain increases.

Keywords: perovskite superlattice, first-principles, strain, cation, piezoelectricity

PACS: 77.55.Px, 77.65.Ly, 77.84.Lf, 78.20.Bh **DOI:** 10.1088/1674-1056/27/2/027701

1. Introduction

Ferroelectric superlattices have been widely studied due to the unusual and controllable properties which give them much potential in micro-electro-mechanical system (MEMS) domain for sensing or energy harvesting.[1,2] In particular, perovskite structures containing $PbTiO_3$ component, which shows better piezoelectric response, mainly include PZT,[3,4] PMN-PT,[5] PIN-PMN-PT,[6] and some $PbTiO_3$-based superlattices.[7–9] In recent years, Niobate ceramics[10,11] such as $NaNbO_3$ and $KNbO_3$, have been studied as promising Pb-free piezoelectric ceramics. Lanthanum aluminate ($LaAlO_3$),[12,13] extensively used as the substrate material for the growth of functional thin films, is a popular target of fundamental investigation, since it exhibits a wide variety of physical and mechanical properties when the applied conditions are changed.

The ferroelectric oxide superlattices present an exciting opportunity for developing novel materials with extraordinary properties; also they are instrumental in studying the fundamental physics of ferroelectric materials. In the studies of complex solid–solution perovskite materials, cation compositional change and cation ordering,[14,15] are the primary tool for designing these materials and a firm understanding of how individual cations contribute to the overall piezoelectric response would help the rational design of high-performance piezoelectric materials. Therefore, studying the contributions of the individual cations to the total piezoelectric response of such superlattices is very important.

In this paper, we change out-plane lattice constant to apply axial strains, noted as Δc, to investigate the polarization and piezoelectric behaviors of the tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices. The associated atomic displacements and Born effective charges are also calculated to explain the origin of the polarization and piezoelectric behaviors. The investigation in this paper can provide theoretical value for the comprehensive understanding piezoelectric response of $PbTiO_3$-based superlattices and research of the high-performance piezoelectric materials.

2. Methodology

We perform first-principles calculations, using pseudopotential framework of density functional theory (DFT)[16,17] for the tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices. All calculations use projector augmented wave (PAW) potential[18] with the Vienna *ab initio* simulation package (VASP),[19–21] and choose the local density approximation (LDA) for the exchange correlation functional. The positions of the ions were relaxed toward equilibrium until the Hellmann–Feynman forces became less than 0.001 eV/Å. A $6\times6\times3$ Monkhorst–Pack *k*-point mesh[22] and 500-eV plane wave cutoff were given to achieve good convergence of computed ground state properties.

As shown in Fig. 1, these are tetragonal structures

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of $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices at the ground state, which consist of B cations at the centers of the oxygen coordinate octahedra and the A cations in the spaces (coordination 12) between the octahedra. The equilibrium structures of the tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices at the ground state are obtained through the constrained structural optimization. In order to study polarization and piezoelectricity behaviors of the individual cations in the tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices accurately, a relatively small Δc (-0.15 Å$\sim +0.15$ Å) with an interval of 0.025 Å is used; and when Δc changes from -0.15 Å to $+0.15$ Å, representing out-plane strain varying from compressive state to tensile state. By applying the strain along the c axis from compressive strain to tensile strain, we conduct the constrained structural optimization until the stress tensor (i.e., σ_{11} and σ_{22}) are all smaller than 0.01 GPa. Then, the corresponding polarization and Born effective charges were calculated by the Berry phase method[23] and density functional perturbation theory, respectively.

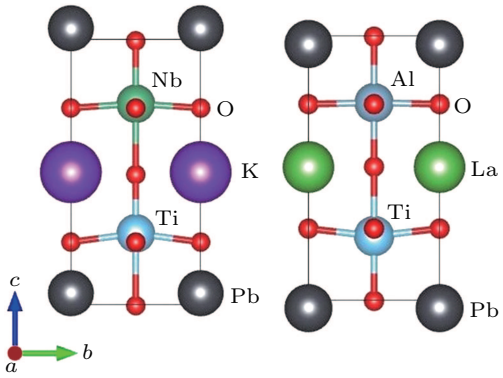


Fig. 1. (color online) The tetragonal structure of (a) $PbTiO_3/KNbO_3$ and (b) $PbTiO_3/LaAlO_3$ superlattices in the ground state.

The A-site and B-site polarization contributions are calculated by formulas $P(\mathrm{A}) = Z^*_{33}(\mathrm{A}) \times D(\mathrm{A})/V$ and $P(\mathrm{B}) = Z^*_{33}(\mathrm{B}) \times D(\mathrm{B})/V$, where $Z^*_{33}(\mathrm{A})$ and $Z^*_{33}(\mathrm{B})$ are the Born effective charges calculated by the density functional perturbation theory, $D(\mathrm{A})$ and $D(\mathrm{B})$ are the off-center displacement of cations from the center of the corresponding O_{12} cage and O_8 cage, and V is the volume of the superlattice. Then the contributions of A-site and B-site atoms to the total piezoelectricity d_{33} can be calculated as $d_{33}(\mathrm{A}) = \partial P(\mathrm{A})/\partial \delta_{33}$ and $d_{33}(\mathrm{B}) = \partial P(\mathrm{B})/\partial \delta_{33}$,[24] where P denotes atomic polarization and δ_{33} is the stress along the c axis of the superlattice.

3. Results and discussions

The calculated lattice constants, Born effective charge, polarization and piezoelectricity d_{33} of the tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices at the ground state are listed in Table 1. The in-plane lattice constant of the tetragonal superlattices is between the two individuals.[25–27] The Born effective charge tensor Z^*_{33} characterizes the influence of long-range Coulomb interactions on the vibrational and optical properties.[28] It is clear that Z^*_{33} of the A- and B-site atoms are relatively larger than their corresponding nominal ionic value, revealing the charge redistribution caused by the dynamic modification of orbital hybridizations.[29,30] According to Table 1, equilibrium lattice constant a of tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices are 3.941 Å and 3.817 Å, so $PbTiO_3$ layer in two superlattices suffers from different strains, inducing different charge transfers between Ti and O atoms in $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices, and there is different Z^*(Ti) in these two superlattices. In $PbTiO_3/KNbO_3$, the charges of the B-site atoms (Ti, Nb) are surprisingly large in the sense that they reach about twice the value they would have in a pure ionic picture, indicating the strong covalent hybridization between O and the transition metal (Ti, Nb).[31,32] Comparing to $PbTiO_3/KNbO_3$, Z^*_{33}(Pb) in $PbTiO_3/LaAlO_3$ increase a little, and Z^*_{33}(Ti) decreases a lot, showing that the strong covalent hybridization between O 2p and Ti 3d orbitals is weakened and the charge transfers between Pb and O increase. Besides, $PbTiO_3/KNbO_3$ shows better polarization and piezoelectric response than $PbTiO_3/LaAlO_3$.

Table 1. Lattice constants (in unit Å), effective charges (in unit e), polarization (in units C/m^2), and d_{33} (in units pC/N) of the ground state of the tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices.

	$PbTiO_3/KNbO_3$	$PbTiO_3/LaAlO_3$
a/Å	3.941[25,26]	3.817[27]
c/Å	8.026	7.669
Z^*_{33}(A1)/e	2.612	3.068
Z^*_{33}(A2)/e	1.309	4.233
Z^*_{33}(B1)/e	8.165	4.872
Z^*_{33}(B2)/e	8.932	3.507
P	0.532	0.202
d_{33}	44.594	13.944

As shown in Fig. 2, Born effective charges Z^*_{33} of the A- and B-site atoms versus c-axis length change (Δc) in superlattices are given. In $PbTiO_3/KNbO_3$ superlattice, Z^*_{33} of the B-site atoms (Ti and Nb atom) declines gradually and the Z^*_{33} of A-site atoms (Pb and K) changes insignificantly as Δc is varied from -0.15 Å to $+0.15$ Å, which indicates strain induces charge transfer from B-site atoms to O atom and little charge transfer from A-site atoms to O atom. The effect of strain on charge transfer of A-site atoms and B-site atoms of $PbTiO_3$ layer is identical to that of $KNbO_3$ layer in $PbTiO_3/KNbO_3$ superlattice. In $PbTiO_3/LaAlO_3$ superlattice, with Δc changing from -0.15 Å to $+0.15$ Å, Z^*_{33}(Ti) of B-site atoms and Z^*_{33}(Pb) of A-site atoms decrease in $PbTiO_3$ layer, while Z^*_{33}(La) of B-site atoms increases a little and Z^*_{33}(Al) of A-site atoms has little change in $LaAlO_3$ layer; showing that strain leads to charge transfer from A-site atom and B-site atom to O atom in $PbTiO_3$ layer, and charge transfer from A-atom to O atom in $LaAlO_3$ layer. The effect of strain on charge transfer in $PbTiO_3$ layer is different from that in $LaAlO_3$ layer.

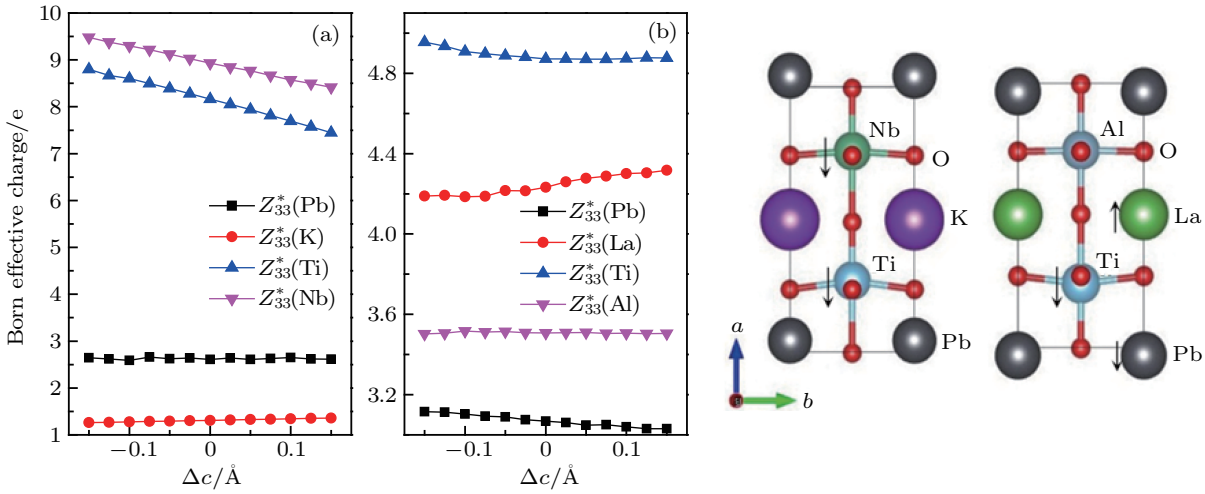


Fig. 2. (color online) The Born effective charges Z^*_{33} in (a) $PbTiO_3/KNbO_3$ and (b) $PbTiO_3/LaAlO_3$ versus c-axis length change.

In Fig. 3, the displacements of the cations from the corresponding O_8 and O_{12} cage center versus c-axis length change (Δc) were calculated in tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices. According to Fig. 3, it is found that, when strain changes from compressive state to tensile state, all atomic displacements from the corresponding O_8 and O_{12} cage center increase gradually, and atomic displacement response to strain in $PbTiO_3/KNbO_3$ superlattices is stronger than that in $PbTiO_3/LaAlO_3$ superlattices. In $PbTiO_3/KNbO_3$ superlattices, compared with K and Nb atoms in $KNbO_3$ layer, Pb and Ti atoms in $PbTiO_3$ layer have larger displacement response to strain because of excellent piezoelectricity in $PbTiO_3$. In $PbTiO_3/LaAlO_3$ superlattices, atomic displacement response to strain of La and Al atoms in $LaAlO_3$ layer is smaller than that of Pb and Ti atoms in $PbTiO_3$ layer. In both superlattices, $PbTiO_3$ layer has the largest atomic displacement response to strain; $KNbO_3$ layer is middle, $LaAlO_3$ layer is smallest.

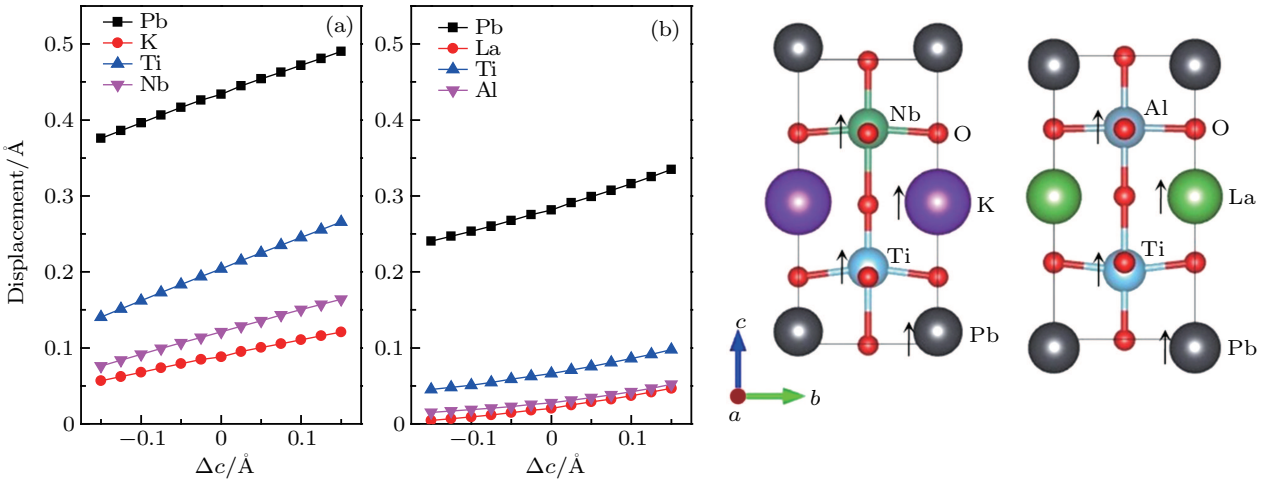


Fig. 3. (color online) The displacement from the center of the corresponding O_{12} cage and O_8 cage in (a) $PbTiO_3/KNbO_3$ and (b) $PbTiO_3/LaAlO_3$ versus c-axis length change.

The polarization of each cation in $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices is indicated in Fig. 4. The atomic polarization is calculated by formulas $P = Z^*_{33} \times D/V$, where Z^*_{33}, D, and V are Born effective charge, the atomic displacement from the corresponding O_8 and O_{12} cage in the axial direction, and volume V of the unit cell, respectively. As indicated in Fig. 4, the polarization of the $PbTiO_3/KNbO_3$ superlattice is larger than that of the $PbTiO_3/LaAlO_3$ superlattice, illustrating that the $PbTiO_3/KNbO_3$ superlattice may have better piezoelectricity than that of the $PbTiO_3/LaAlO_3$ superlattice. With Δc varying from -0.15 Å to $+0.15$ Å, both total polarization of superlattices and polarization of each cations increase gradually, and polarization of $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices raise from 0.42 C/m^2 to 0.63 C/m^2 and from 0.15 C/m^2 to 0.27 C/m^2, respectively. Polarization from B-site is significant because of the strong hybridization between Ti 3d (Nb 4d) orbitals and O 2p orbital, while the A-site atoms (Pb and K) have a relatively lower Born effective charge. Pb atom contributes more to the total polarization because displacement and Born effective charge of the

Pb atom is larger than those of the K atom. The weak polarization contribution of K atom ascribes to its small displacement and Born effective charge. Besides, the rate of change of P(Ti) and P(Nb) is bigger than that of P(Pb)and P(K) in response to the c-axis strain. For the tetragonal $PbTiO_3/KTaO_3$ and $PbTiO_3/LaAlO_3$ superlattices, P(Pb,Ti) in the $PbTiO_3$ layer has larger contribution to the total polarization than P(K,Nb) in the $KNbO_3$ layer and P(La,Al) in the $LaAlO_3$ layer.

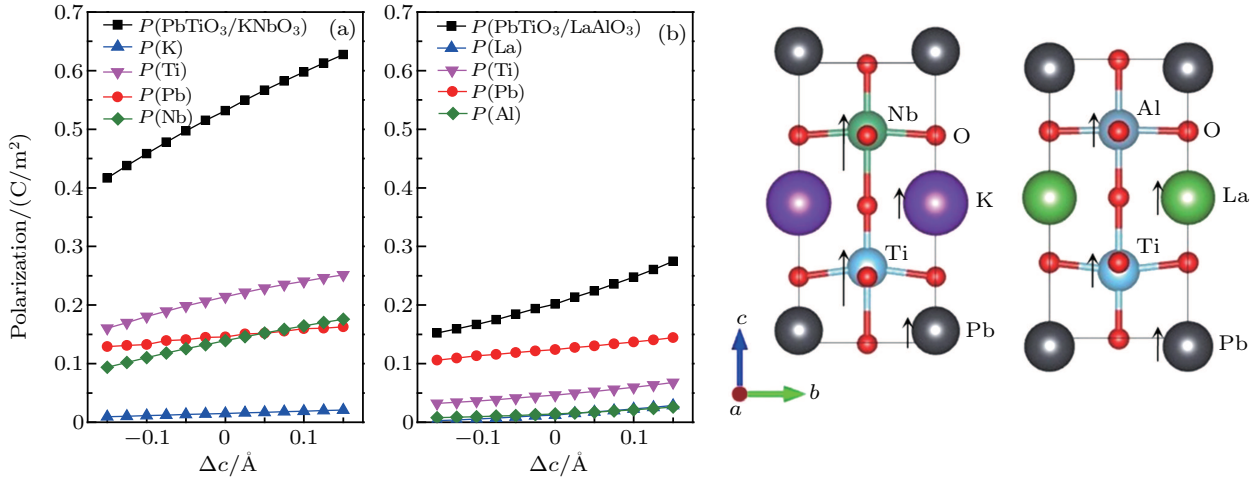


Fig. 4. (color online) The polarization distributions in (a) $PbTiO_3/KNbO_3$ and (b) $PbTiO_3/LaAlO_3$ versus c-axis length change.

Lastly, the axial stress σ_{33} of $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ versus c-axis length change (Δc) are calculated, as indicated in Fig. 5. It is shown that the variation trend of σ_{33} versus c-axis strain is very similar. The value of σ_{33} decreases slowly to around zero, then increases inversely. But for the same c-axis length change Δc, σ_{33} in the $PbTiO_3/KNbO_3$ superlattice is smaller than that in the $PbTiO_3/LaAlO_3$ superlattice.

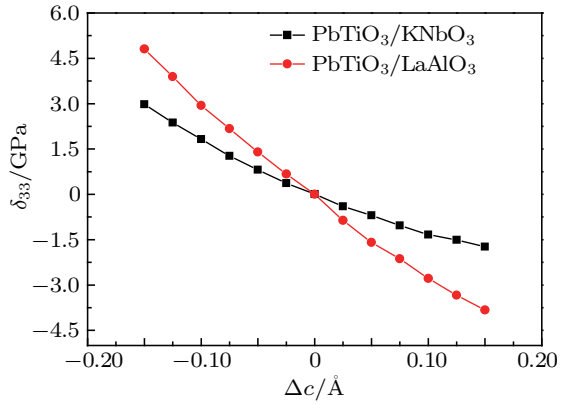


Fig. 5. (color online) The σ_{33} of (a) $PbTiO_3/KNbO_3$ and (b) $PbTiO_3/LaAlO_3$ versus c-axis length change.

Through formulas $d_{33}(\mathrm{A}) = \mathrm{d}P(\mathrm{A})/\mathrm{d}\sigma_{33}$ and $d_{33}(\mathrm{B}) = \mathrm{d}P(\mathrm{B})/\mathrm{d}\sigma_{33}$, we gain the piezoelectric response d_{33} of each cation in $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices in Fig. 6. As the c-axis length change (Δc) changes from -0.15 Å to $+0.15$ Å, in two superlattices, both total d_{33} and contributions from all cations increase continually, and the trend is more significant in the tensile state. In the $PbTiO_3/KNbO_3$ superlattice, there is a significant gap between the d_{33}(A) and d_{33}(B), and the total d_{33} increases from 37.07 pC/N to 75.64 pC/N, and the piezoelectric contributions from B-site atoms (Ti, Nb) is larger than that from A-site atoms (Pb, K). In the $PbTiO_3/LaAlO_3$ superlattice, the total d_{33} increases from 7.86 pC/N to 25.76 pC/N, and the piezoelectric contribution almost comes from Pb and Ti in the $PbTiO_3$ component, and the difference between d_{33} (La) and d_{33} (Al) is very minor. In particular, in the compressive c-axis condition, d_{33} (Pb) contributes most to the total d_{33}. It is concluded that there is the largest piezoelectric contribution of $PbTiO_3$layer to the total d_{33} and the smallest piezoelectric contribution of $LaAlO_3$ layer to the total d_{33}, which indicate that the total d_{33} of $PbTiO_3/KNbO_3$ superlattice is bigger than that of the $PbTiO_3/LaAlO_3$ superlattice.

In order to investigate the influence of the component $PbTiO_3$ to the piezoelectric response of $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ superlattices, the proportion of the piezoelectric contributions from $PbTiO_3$ component in the superlattices is calculated, as shown in Fig. 7. The proportion is around 60% at the ground state of the tetragonal superlattices, and the proportion shows different responses to the c-axis strain but still with a value larger than 50%. In the $PbTiO_3/KNbO_3$ superlattice, as strains change from compressive state to tensile state, the proportion of $PbTiO_3$ layer first increases and then decreases, and reaches maximum near the equilibrium state. However, in $PbTiO_3/LaAlO_3$ superlattices, the c-axis strain increases the proportion, especially in the compressive state. In two superlattices, the proportion of the piezoelectric contributions from $PbTiO_3$ component in the $PbTiO_3/LaAlO_3$ superlattice is larger than that of the $PbTiO_3/KNbO_3$ superlattice, because of small piezoelectric contribution of La and Al atoms.

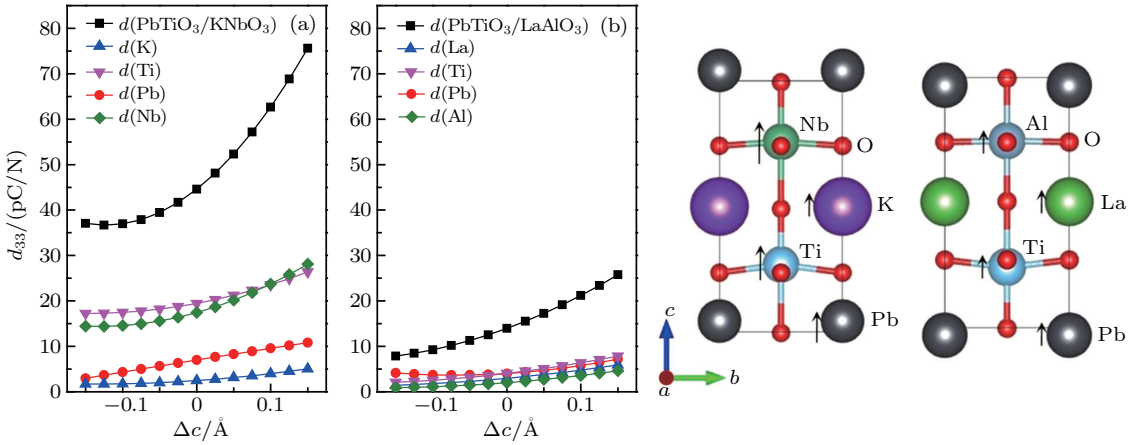


Fig. 6. (color online) The d_{33} piezoelectric distributions in (a) $PbTiO_3/KNbO_3$ and (b) $PbTiO_3/LaAlO_3$ versus c-axis length change.

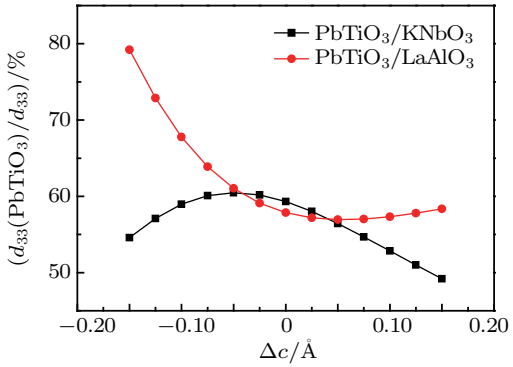


Fig. 7. (color online) The proportion of the piezoelectric contributions from $PbTiO_3$ component in $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ versus c-axis length change.

4. Conclusion

In this paper, we performed a first-principles study on the polarization and piezoelectric behaviors of the tetragonal $PbTiO_3/KNbO_3$ and $PbTiO_3/LaAlO_3$ as a function of c-axis length change. The contributions of the A-site and B-site atoms to polarization and the total d_{33} are discussed. In $PbTiO_3/KNbO_3$ superlattices, the B-site atoms make relatively larger contributions to polarization and the total d_{33} than the A-site atoms because of the strong covalent interactions between the transition metal (Ti, Nb) and the oxygen atoms, which is demonstrated by the large dynamic charge transfers between Nb 4d, Ti 3d orbitals, and O 2p orbitals. The A-site atom Pb has a relatively larger polarization and piezoelectric contribution than K due to more intensive interaction between Pb and O atoms and the huge offset displacement. Meanwhile in $PbTiO_3/LaAlO_3$ superlattices, contributions from the B-site atoms are weakened because of the weak contribution from Al atom, highlighting the influence from A-site atom Pb which has a huge offset displacement. By analyzing the proportion of the piezoelectric contributions from $PbTiO_3$ component in the superlattices, the influence from $PbTiO_3$ component is weakened in $PbTiO_3/KNbO_3$ as the c-axis strain is applied. However, in the $PbTiO_3/LaAlO_3$ superlattice, the $PbTiO_3$ component plays a leading role to the total d_{33}, especially in the compressive strains, and the proportion decreases as the tensile strains increase.

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